

Analysis of a High-Efficiency Natural Gas-Assisted Steam Electrolyzer for Hydrogen Production

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ANALYSIS OF A HIGH-EFFICIENCY NATURAL GAS-ASSISTED STEAM ELECTROLYZER FOR HYDROGEN PRODUCTION

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ABSTRACT

This paper presents a description and analysis of a high-efficiency hydrogen production system. The main component of the system is a novel steam electrolyzer. In conventional electrolyzers, oxygen produced from electrolysis is usually released into the environment. In this design, natural gas is used to react with the oxygen produced in the electrolysis, reducing the chemical potential difference across the electrolyzer, thus minimizing electricity consumption. The oxygen produced from the electrolysis is consumed in either a total oxidation or a partial oxidation reaction with natural gas. Experiments performed on single cells shown a voltage reduction as much as 1 V when compared to conventional electrolyzers. A heat recovery system (heat exchangers and catalytic converter) has been incorporated to the electrolyzer to obtain a high efficiency hydrogen production system. Results from a thermodynamic analysis show up to 70% efficiency with respect to primary energy source.

NOMENCLATURE

H	Absolute Enthalpy (includes enthalpy of formation)
m	Mass
E_{elec}	Electrical energy
ϵ_p	Preheater effectiveness
ϵ_c	Condenser effectiveness
ϵ	Heat exchanger effectiveness
η	Efficiency
η_{elec}	Efficiency of electricity generation
T	Temperature, K
LHV	Lower heating value
Subscripts	
CH ₄	Methane
H ₂	Hydrogen

INTRODUCTION

Hydrogen is one of the leading candidates in the search for an alternative to fossil hydrocarbon fuels. Hydrogen can be made from a diverse range of sources, reducing the economic, political, and

environmental costs of energy systems. In the long term, hydrogen from renewable sources offers the potential of sustainable energy infrastructure.

Hydrogen is an energy carrier like electricity and can be produced from a wide variety of energy sources, such as natural gas, coal, biomass, solar (thermal and photovoltaic), wind, hydroelectric, as well as sewage, municipal solid waste, tires, and discarded oil [2]. The U.S. market for hydrogen is currently more than 0.7×10^{18} J/yr (equivalent in energy to 115 million barrels of oil), with 60% being used in the production of ammonia. In addition, a comparable amount is produced and used in petroleum refineries [3].

Hydrogen has the highest energy content by weight of any fuel and will quickly disperse if accidentally spilled or released. It also allows combustion at the high compression ratios and efficiencies in internal combustion engines [4]. When combined with oxygen in electrochemical fuels, hydrogen can produce electricity directly, bypassing the Carnot cycle efficiency limits of today's power plants and internal combustion engine generators.

Hydrogen offers a number of features that make it a serious candidate as a 21st century vehicular fuel. However, hydrogen vehicles will not be used in significant numbers until there is a reliable hydrogen supply infrastructure. An important part of this infrastructure is the development of more efficient hydrogen production systems. Presently almost all the hydrogen demand is met by hydrogen made in steam reforming of natural gas. Another option is production of hydrogen by water electrolysis. However, this is expensive due to the high consumption of electrical energy.

Conventional electrolysis plants have about 75% efficiency with respect to electrical energy input [5]. Typical efficiencies for thermal power plants, which generate most of the electricity in the U.S., are in the range of 35-40% [5]. The total thermal efficiency of hydrogen production is therefore in the range of 26-30% [5]. This efficiency will grow in the future, but it is unlikely to reach very much above 40% [5].

Hydrogen production by high temperature electrolysis of water vapor using solid-oxide electrolyte cells has been demonstrated to be a very efficient method, with 39-44% efficiency for 38% efficiency of electrical energy generation [6, 7, 8, 9]. Efficiency is higher than

the efficiency of power generation because a fuel is used directly to generate steam at the operating temperature, therefore reducing the electricity consumption. Doenitz et al. [9] predicts a maximum efficiency of hydrogen production of over 50% by using this technology.

The main drawback of electrolyzers is the high electricity consumption. Electricity is known to be the most expensive form of energy. As a result, electrolytic hydrogen is more expensive than the steam-reformed hydrogen by a factor of at least two to three [9]. Moreover, electricity is not a primary energy but must be produced using fossil fuels, nuclear fuels or renewable energy. Considering the fact that the production of electricity has an average efficiency of less than 40% with respect to primary energy, the overall efficiency of the electrolyzer is low. In addition, currently, less than 30% of the overall electricity production in the United States involves renewable or nuclear energy. As a consequence, electrolysis using electricity coming from the grid is not a carbon-free process, but actually involves a large amount of greenhouse gases due to the use of electricity that is mostly produced from burning coal and natural gas.

The long-term objective of this project is to develop a high efficiency steam electrolyzer for carbon-free production of hydrogen. However, this can only be accomplished when renewable energy and nuclear become the major sources of electricity production. In the meantime, the short-term goal is to develop a transitional electrolyzer technology that takes into account the current situation of electricity production and the current economic infrastructure. The goal for the transitional electrolyzer technology is a distributed hydrogen production system with lower electricity consumption, higher overall efficiency and lower greenhouse gas emissions.

This paper describes a new concept of electrolyzer and presents the thermodynamic analysis of a hydrogen production unit that has as a main component the novel electrolyzer and a heat recovery system. The next two sections describe the electrolyzer and the heat recovery system.

NATURAL GAS-ASSISTED STEAM ELECTROLYZER (NGASE)

Background

Water is best electrolyzed at high temperatures (700-1000°C) where the high temperature accelerates the reaction kinetics, reducing the energy loss due to electrode polarization, thus increasing the overall system efficiency. In addition, preheating of the steam can be obtained by heat recovery or by fuel burning [9]. Typical high temperature electrolyzers such as the German HOT ELLY system achieve 92% in electrical efficiency while low temperature electrolyzers can reach at most 85% efficiency [9]. Despite this high efficiency with respect to electricity, the German system still produces hydrogen at about twice the cost of steam-reformed hydrogen [9]. According to the analysis of the HOT ELLY system, about 80% of the total hydrogen production cost comes from the electricity cost [9]. Therefore, to make the electrolytic hydrogen competitive with the steam-reformed hydrogen, the electricity consumption of the electrolyzer must be reduced. Currently, there is no solution because the high electricity consumption is dictated by the thermodynamics of water decomposition.

In conventional steam electrolyzers, the gas that circulates in the cathode side (where water is decomposed) is usually a mixture of steam and hydrogen, while the gas circulating in the anode side is oxygen. At zero current, the system has an open-circuit voltage of

0.8 to 0.9 V, depending on the hydrogen/steam ratio and on operating temperatures. In order to electrolyze water, a voltage higher than the open circuit voltage must be applied in order to pump oxygen from the steam side to the oxygen side. Clearly, much of the electricity used, 60 to 70% of the total electric power, is used in forcing the electrolyzer to operate against the high chemical potential gradient for oxygen.

In order to lower the open circuit voltage, and thus the electricity consumption, natural gas can be circulated in the anode [11]. The reducing character of natural gas will help to bring down the chemical potential difference between the two sides of the electrolyzer. There are two different modes of operation: total oxidation or partial oxidation of natural gas. In the first case, natural gas is used in the anode side of the electrolyzer to burn out the oxygen coming from the electrolysis, thus reducing or eliminating the potential difference across the electrolyzer membrane. The products of the reaction will be CO₂ and steam. The role of natural gas is to lower the chemical potential gradient, therefore reducing the electricity consumption. This mode replaces one unit of electrical energy by one equivalent energy unit of natural gas at one-fourth the cost. For thermodynamic reasons, the total oxidation mode is restricted to temperatures lower than 700°C. Above 800°C, carbon monoxide becomes more stable and total oxidation is not possible.

In the partial oxidation mode, an appropriate catalyst on the anode side will promote the partial oxidation of natural gas to carbon monoxide and hydrogen. The resulting gas mixture, also called syngas, can be used in important industrial processes such as the synthesis of methanol, liquid fuels, etc. Most important of all, CO can also be shifted to CO₂ to yield additional hydrogen. In this process, hydrogen is produced at both sides of the steam electrolyzer. The overall reaction is equivalent to the steam reforming of natural gas. As opposed to steam reforming reactors, the modular characteristics of the electrolyzer, along with the absence of the extensive heat exchangers, makes it possible to build small-scale hydrogen production units. However, we chose to focus our effort on the total oxidation mode because it is simpler and does not require any additional water shift nor CO clean-up units.

In both cases, the key point of the approach is to use natural gas directly in the electrolyzer instead of using natural gas to make electricity at the central plant and then to use that electricity to split water. The efficiency and the carbon emissions will be lower than in conventional electrolysis. The NGASE is not a carbon free hydrogen production system because it still involves natural gas. However, by combining both natural gas and electricity, which have existing infrastructures, the NGASE is an ideal transitional technology for distributed hydrogen production.

Design of the NGASE Electrodes

Early characterization has shown that the anode performance is mainly diffusion-limited. Therefore, improving the anode porosity should improve the gas phase diffusion and thus the anode performance. Various pore former materials, including carbon, polymers and starches have been tested. The optimum pore former amount has also been identified. Figures 1a and 1b shows the Scanning Electron Microscopy (SEM) pictures of the cross-section view of the anode materials without (1999 cell design) and with pore former (2000 cell design) respectively. The black dots correspond to the pores. Clearly, the sample in Figure 1b is significantly more porous than sample in Figure 1a. The pores introduced are homogeneous and uniformly distributed in the matrix of the anode.

Figure 2 shows the performance of the new cells with optimum porosity. The I-V curve of the HOT ELLY steam electrolyzer [9] as well as that of a previous design data is reproduced for comparison. The performance of the 1999 NGASE cell is similar to that of the HOT ELLY as indicated by the same slope. However, the voltage is about 1 V lower due to the use of methane depolarizer. The 2000 NGASE cell with optimum anode porosity outperforms the other cells. At only 0.5 V, the electrolytic current is as high as 2.8 A/cm², compared to 1 A/cm² for the 1999 cell. The introduction of pore former has thus improved the electrolytic current by almost a factor of three. This is probably the highest electrolytic current per unit area ever reported to date.

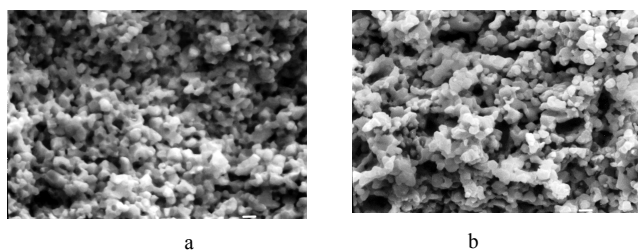


Figure 1 – SEM pictures of: a. 1999 anode with low porosity, b. 2000 anode with optimized porosity

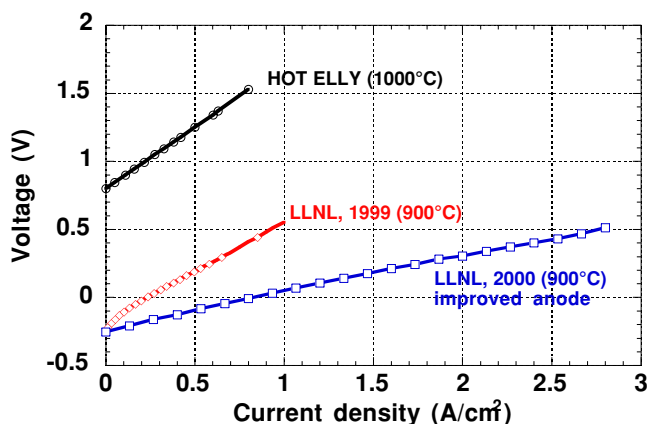


Figure 2 – Current-Voltage characteristics of various steam electrolyzer cells

The problem with operating at 900°C is that it is necessary to introduce steam in the methane side in order to avoid carbon deposition. The presence of excess steam can cause excessive steam-reforming of methane, which is undesirable because of the reaction is highly endothermic. Thus, it is highly desirable to reduce the operating temperature to minimize the amount of steam and also to favor the total oxidation of methane. Figure 3 shows the I-V plot of the new cell with improved anode at 700°C. The performance drops significantly, the electrolytic current at 0.5 V is down from 2.8 A/cm² at 900°C to 0.35 A/cm². This poor performance has been identified as due essentially to the cathode. The cathode material, Ni/YSZ, was

then replaced with a better electrode/catalyst. The I-V curve of the cell with both improved anode and cathode is also shown in Figure 3. At 0.5 V, the current increases to 1 A/cm², about three times the current of the cell with the old cathode. Overall, the development of the improved cathode and anode has allowed reducing the operating temperature from 900°C to 700°C while preserving excellent cell performance. The main advantage is that carbon deposition is suppressed even with steam concentration as low as 10%.

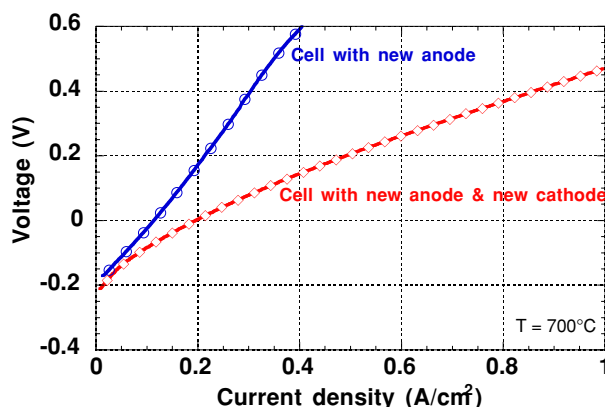


Figure 3 – Current-Voltage characteristics at 700°C

Design of the Electrolyzer Stacks

Most of the current uses of hydrogen require hydrogen under some pressure. Thus the cost consideration of various hydrogen production methods must take into account the need to pressurize hydrogen. If hydrogen is produced at low pressure and a hydrogen compressor is used for pressurization, then the overall production cost could be high due to the high cost, high maintenance and low reliability of the hydrogen compressors.

As mentioned above, pure electrolysis is not attractive due to the high electricity consumption from the hydrogen production standpoint. However, electrochemical devices are known to be the most efficient devices for the pressurization of hydrogen. One of the most attractive features is that electrochemical compressors only require an extra ~100 mV to pressurize hydrogen from ambient pressure to 34.5 MPa (5000 psi). Therefore, the design of the electrolyzer stack must take advantage of the possibility to pressurize hydrogen in-situ.

Since the electrolyzer is basically a fuel cell operating in reverse mode, the various stack designs developed for fuel cells can be considered for use for the electrolyzer. There are two major stack designs: tubular or planar configurations. The planar configuration can be made compact and is potentially cheaper than the tubular design. However, planar stacks are much more difficult to pressurize because they are more subject to mechanical fractures due to differences in pressures between the sides. For this reason, we chose to pursue the tubular configuration since this design allows pressurizing the exterior compartment while having ambient pressure inside the tubes. Figure 4 shows a drawing of the tubular electrolyzer stack with four tubes. The electrolyzer stack is located inside a metal vessel that can withstand high pressures. Natural gas flows inside the tubes at ambient pressure while the outside compartment is exposed

to steam/hydrogen mixture at high pressure. Figure 5 shows the experimental reactor where the electrolyzer stack will be tested. Although the objective for this analysis is for hydrogen production at ambient pressure only, the system was designed for pressure operation up to 1 MPa (150 psi) for future research work.

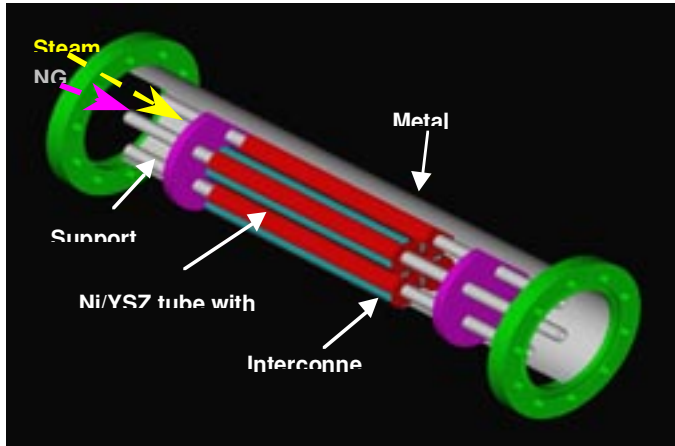


Figure 4 – Drawing of a four-tube electrolyzer stack



Figure 5 – Bench-scale reactor for a 100 W electrolyzer stack

Tube Fabrication Process

A complete tube fabrication process has been developed. Nickel oxide/yttria stabilized zirconia (NiO/YSZ) anode support tubes were made by cold isostatic pressing or by extrusion. The green tube was masked, and an interconnect thin film was deposited in form of a thin stripe along the tube. YSZ electrolyte thin film was then coated on the tubes, followed by sintering at high temperatures [10]. The thin film cathode was subsequently deposited. All thin films were processed using the Colloidal Spray Deposition, a low cost thin film deposition technique that we have developed recently [11]. Figures 6a and 6b show the tube after cold isostatic pressing and after completion respectively. A SEM cross-section view of the

electrolyzer tube is shown in Figure 7. The performance of the individual tubes is currently being evaluated.



Figure 6 - Electrolyzer tubes: a. green tube after cold isostatic pressing, b. after completion

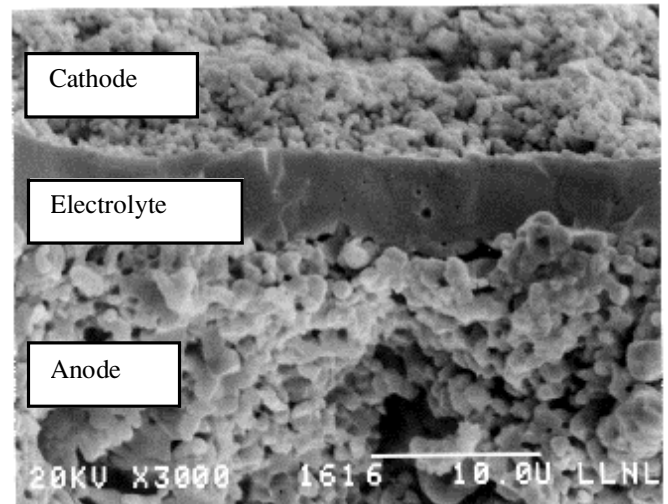


Figure 7 – SEM cross-section view of an electrolyzer tube

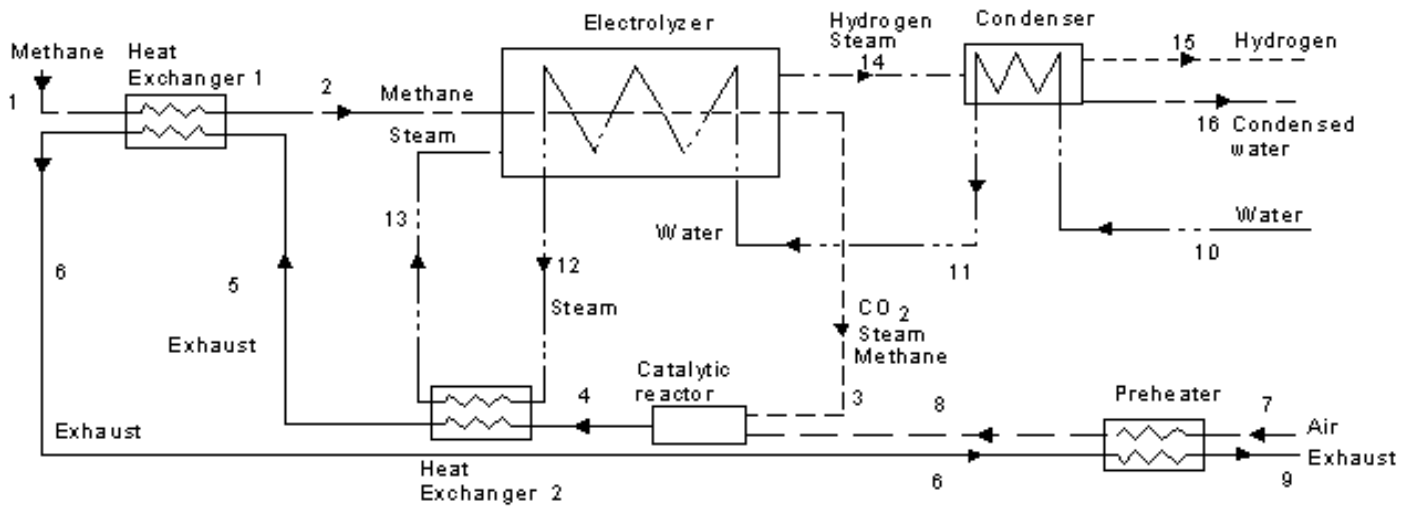
HEAT RECOVERY SYSTEM

A conceptual design of a heat recovery system has been developed. Heat exchangers and catalytic converter has been added to the electrolyzer unit to recover heat from the exhaust gas and to burn the methane that is not oxidized in the electrolyzer.

The electrolyzer is designed to work at 700°C. Inlet temperatures for the methane and steam should also be close to 700°C for high efficiency. This may be accomplished by recovering heat from the combustion products using heat exchangers. In addition to this, not all the methane can be oxidized in the electrolyzer. The maximum fraction of methane that can be burned in the electrolyzer is 80-90%. A catalytic reactor is therefore incorporated into the system to take advantage of the energy of combustion of the remaining methane.

Figure 8 shows a schematic of the conceptual design of the electrolyzer and heat recovery system for hydrogen production. First, methane goes through a heat exchanger where it is heated to 700°C (the electrolyzer temperature) by recovering energy from the exhaust stream. This hot methane then enters the anode section of the electrolyzer. Part of the methane (70-90%) is oxidized in the electrolyzer with the oxygen generated from the electrolysis in the cathode side. The analysis of this system assumes that the only exhaust anode gases are CO₂, steam, and methane (point 3, Figure 8). This mixture enters a catalytic reactor to burn the remaining methane. The air necessary to burn the methane in the catalytic reactor is heated in the preheater by using the energy of the exhaust gas. The

electrolyzer to remove the thermal energy generated by methane combustion. The water leaves the electrolyzer as high-temperature steam (point 12, Figure 8). The water is further heated to the electrolyzer temperature by exchanging heat with the catalytic reactor exhaust (point 13, Figure 8). In this analysis the electrolyzer temperature is 700°C. Points 2, 3, 13, and 14 in Figure 8 are also at the electrolyzer temperature.



ANALYSIS

Heat Exchanger 1

$$\mathcal{E}_1 = \frac{H_2 - H_1}{H_5^* - H_1} \quad (1)$$

Heat Exchanger 2

$$\varepsilon_2 = \frac{H_{13} - H_{12}}{H_4^* - H_{12}} \quad (2)$$

Condenser

$$\mathcal{E}_c = \frac{H_{11} - H_{10}}{H_{14}^* - H_{10}} \quad (3)$$

The equation of conservation of energy in the electrolyzer, considering no heat loses, is

$$E + H_2 + H_{13} + H_{11} = H_{14} + H_3 + H_{12} \quad (4)$$

$$H_4 = H_3 + H_8 \quad (5)$$

$$\varepsilon_p = \frac{H_8 - H_7}{H_6^* - H_7} \quad (6)$$

where H_6^* is the absolute enthalpy of the air at the temperature of port 6.

Finally, the efficiency of the system in terms of primary energy is calculated as,

$$\eta = \frac{m_{H_2} LHV_{H_2}}{m_{CH_4} LHV_{CH_4} + \frac{E_{elc}}{\eta_{elc}}} \quad (7)$$

and the efficiency of the system based on total energy into the electrolyzer is,

$$\eta = \frac{m_{H_2} LHV_{H_2}}{m_{CH_4} LHV_{CH_4} + E_{elc}} \quad (8)$$

This system of equation is solved with an iterative equation solver by using computer-based tables of properties for all the substances involved (water, oxygen, nitrogen, methane and hydrogen).

RESULTS

Table 1 shows the values of the system parameters used in the analysis. Figure 9 shows the efficiency of the system with respect primary energy (Equation 7), as a function of current density in the electrolyzer, assuming 40% efficiency for electricity generation. The figure also shows the voltage across the electrolyzer as a function of current density. Figure 9 shows that as the current density is decreased, the voltage in the fuel cell drops, as previously shown in Figure 3. Therefore, electricity consumption drops for lower current density and the efficiency of the system increases. This gain in efficiency is obtained at the expense of reducing the rate of production of hydrogen in the system. A larger, more expensive electrolyzer can generate hydrogen at a higher efficiency with less methane consumption by reducing the electrolyzer loading. An optimum current may be determined from economics, by balancing the cost of fuel consumed with the capital cost of the electrolyzer.

Table 1. System parameters considered in this analysis

System Parameter	Symbol	Value
Preheater effectiveness	ε_p	0.85
Condenser effectiveness	ε_c	0.80
Heat exchanger 1 and 2 effectiveness	$\varepsilon_1, \varepsilon_2$	0.85
Electrolyzer temperature	T_e	973 K
Methane lower heating value [12]	LHV_{CH_4}	50MJ
Hydrogen lower heating value [12]	LHV_{H_2}	120MJ

Figure 9 also shows system efficiency for three fractions of methane utilization: 0.7, 0.8, and 0.9. $U=0.8$ indicates that 80% of the

methane that enters the electrolyzer is oxidized inside the electrolyzer and the remaining is oxidized in the catalytic reactor. The figure shows that as methane utilization increases, the system efficiency also increases. Clearly, it is more efficient to use the methane directly in the electrolyzer rather than burning it in the catalytic reactor to preheat air. However, a practical limit of the methane utilization in the electrolyzer may be 90%.

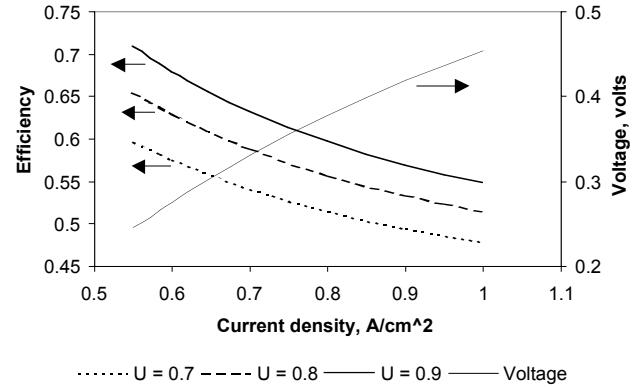


Figure 9. Efficiency (with respect to primary energy source, Equation 7) of the hydrogen production system for three values of methane utilization (0.7, 0.8 and 0.9) as a function of current density in the electrolyzer. The figure also shows operating voltage of the electrolyzer as a function of current density.

Figure 10 shows efficiency of the system with respect to total energy into the system (Equation 8). The efficiency shown in Figure 10 is much higher than in Figure 9, because Figure 10 does not take into account energy lost in the electric power plant. The efficiency in Figure 10 also increases with the decrease of the current density, although the slope of the lines is smaller due to the lower value of electricity (energy losses in the power plant are not considered). Figure 10 also shows system efficiency for three fractions of methane utilization: 0.7, 0.8, and 0.9. Again, the efficiency increases as methane utilization in the system increases.

CONCLUSIONS

This paper presents a description and analysis of a high-efficiency hydrogen production system. The main component of the system is a novel steam electrolyzer. In conventional electrolyzers, oxygen produced from electrolysis is usually released into the environment. In this design, natural gas reacts with the oxygen produced in the electrolysis, reducing the chemical potential difference across the electrolyzer, thus minimizing electricity consumption. The oxygen produced from the electrolysis is consumed in either a total oxidation or a partial oxidation reaction with natural gas. Experiments performed on single cells shown a voltage reduction as much as 1 V when compared to conventional electrolyzers.

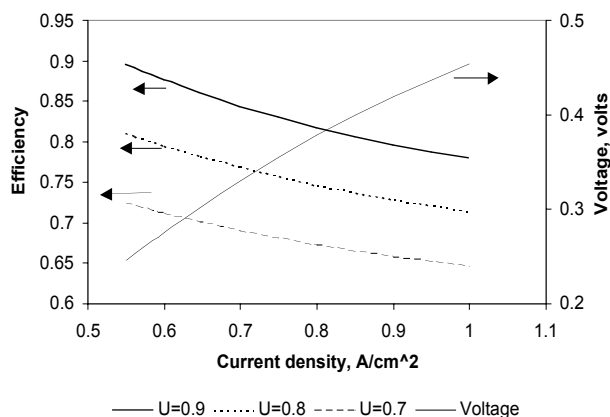


Figure 10. Efficiency (with respect to total energy into the electrolyzer, Equation 8) of the hydrogen production system for three values of methane utilization (0.7, 0.8 and 0.9) as a function of the current density in the electrolyzer. The figure also shows operating voltage as a function of current density.

A heat recovery system (heat exchangers and catalytic converter) has been incorporated to the electrolyzer to obtain a high efficiency hydrogen production system. The system has been analyzed by using a set of equation describing the system components. The set of equations is solved with an iterative solver that includes computerized tables of properties for all the substances that circulate through the system. The thermodynamic analysis shows that the system can reach up to 70% efficiency based on primary energy, or up to 90% efficiency based on total energy input into the electrolyzer. Efficiency is observed to increase as the fraction of methane utilization in the electrolyzer is increased. The efficiency also increases as the current density in the electrolyzer is decreased. Conventional pure electrolysis systems have a maximum efficiency of 75% respect to electrical energy input, and 30% efficiency with respect to primary energy. The NGASE hydrogen production system exceeds considerably the efficiency of the other hydrogen system production developed up to date.

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